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Electrochemical Properties of the Ionic Liquid 1-Ethyl-3-methylimidazolium Difluorophosphate as an Electrolyte for Electric Double-Layer Capacitors

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The electrochemical properties of 1-ethyl-3-methylimidazolium difluorophosphate ($EMImPO_2F_2$) ionic liquid have been investigated as an electrolyte for electric double-layer capacitors using activated carbon electrodes. A two-electrode cell test reveals that the capacitance of $EMImPO_2F_2$ exhibits a larger voltage dependence than that of a typical ionic liquid electrolyte $EMImBF_4$. At a charging voltage of 2.5 V, the capacitance obtained for $EMImPO_2F_2$ is 49 F g^{-1} and is larger than 44 F g^{-1} obtained for $EMImBF_4$. According to the charge–discharge cycle test, the breaking-up voltage of $EMImPO_2F_2$ is lower than that of $EMImBF_4$, which may be caused by the lower anodic stability of $PO_2F_2^-$ than that of BF_4^-. The ionization potential of $PO_2F_2^-$ was calculated by quantum mechanical calculations to estimate its anodic stability and was compared with those of several anions used in typical electrolytes. The results indicate that the anodic stability of $PO_2F_2^-$ is similar to that of ClO_4^- and lower than those of BF_4^- and PF_6^-.
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Electric double-layer capacitors (EDLCs) are attractive energy storage devices for energy regeneration. High power density and long lifetime are the beneficial points of EDLCs compared to secondary batteries because EDLCs store energy at the interface between the electrode surface and the electrolytic solution (or electrolyte) without faradaic processes.[1-4] Electrode materials with a high surface area such as the activated carbon are required for this purpose, whereas the capacitance is usually nonlinear to the specific surface area because of the effect of the pore structure.[5]

Although aqueous electrolytes such as sulfuric acid are attractive in terms of their high conductivity, high capacitance, easy handling, and low cost, the low breaking-up voltage (<1 V for a practical cell) limits their available energy density. The temperature range in which the aqueous electrolyte is usable below and above room temperature is not wide due to relatively high freezing and low boiling temperatures of water. Although the high achievable voltage for nonaqueous electrolytes (~3 V) is a great benefit, their low conductivity increases the internal resistance. From the viewpoint of safety, the flammability of the organic electrolytes is another drawback especially for their application to large-scaled capacitors. Ionic liquids composed of only ionic species have some unique properties such as nonflammability, low vapor pressure, and wide liquid-phase temperature range, rendering the construction of safe electrochemical devices operable in a wide temperature range.[6-10] Their ionic conductivity and electrochemical stability depend on the ionic species, sometimes being comparable to or higher than the organic electrolytes. The use of ionic liquids as electrolytes combined with carbonaceous electrodes in EDLCs has been attempted by many groups, where the fluoroanions [BF_4^-,[11-19] PF_6^-,[11,16] $N(SO_2CF_3)_2^-$,[11,16,20,21] and $N(SO_2F)_2^-$,[22] and others[23,24]] are often used as counteranions. Although the understanding of the double-layer structures in ionic liquids is still undergoing, experimental and theoretical approaches have been made by several research groups.[25-33]

A series of ionic liquids based on the difluorophosphate anion ($PO_2F_2^-$) reported recently exhibits some desirable properties as an electrolyte for EDLCs such as a low melting point, low viscosity, high conductivity, and high hydrolytic stability.[34] The effect of the asymmetric structure for $PO_2F_2^-$ on capacitance should also be examined in comparison with the other highly symmetric anions such as BF_4^- and PF_6^-. In this study, the electrochemical properties of the ionic liquid 1-ethyl-3-methylimidazolium difluorophosphate ($EMImPO_2F_2$, Fig. 1) as an electrolyte for EDLCs are reported.

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Experimental

Reagents.— The ionic liquid electrolyte $EMImBF_4$ was purchased from Kanto Kagaku and dried under vacuum (<1 Pa) at 373 K for 2 days. The starting chloride EMImCl was prepared by the reaction of 1-methylimidazole (Aldrich Chemicals, purity >99%) and chloroethane (Wako Chemicals, purity >99%) and was purified by recrystallization from acetonitrile by adding ethylacetate.[34] The potassium salt KPO_2F_2 was prepared by the reaction of KPO_3 (Wako Chemicals) and KPF_6 (Aldrich purity >99.5%).[34] The difluorophosphate ionic liquid $EMImPO_2F_2$ was prepared by the reaction of EMImCl and KPO_2F_2 and was purified through the activated alumina column as described in the literature.[34] Final drying was performed under vacuum (<1 Pa) at 373 K for 1 week. The Karl–Fischer measurements showed that the typical water contents in these ionic liquids were below 100 ppm.

Measurements.— An electrochemical measurement was performed at 298 K with the aid of an electrochemical measurement system HZ-3000 (Hokuto Denko). The electrochemical window was measured using a vitreous carbon working electrode and a Pt counter electrode. The reference electrode was made of silver wire immersed in $EMImBF_4$, containing 0.05 M $AgBF_4$ that was separated from the electrolyte by a window made of porous Vycor glass. The potential was referenced to the ferrocenium/ferrocene (Fc^+/Fc) redox couple.

A two-electrode cell made of poly(tetrafluoroethylene) (PTFE) was used for the EDLC tests. A pair of activated carbon sheets with a diameter of 10 mm, a thickness of 0.5 mm, and a weight of 0.021 g [85 wt % of activated carbon from phenol resin (surface area, 2050 m^2 g^{-1}, mean pore diameter, 2.14 nm, and total pore volume, 1.10 cm^3 g^{-1}), 10 wt % of PTFE, and 5 wt % of carbon black] were used as electrodes. The electrodes dried under vacuum at 453 K overnight were immersed in the electrolyte and degassed under vacuum before use. The PTFE filter (ADVANTEC H100A013A, 35 μm thickness and 13 mm diameter) was used as a separator. Vitreous carbon disks were used as current collectors. The test cell was charged to a given voltage and discharged at a constant current rate of 5 mA. The capacitance C (F g^{-1}) was calculated from the discharge curve using the relationship $C = it/wV$, where i is the current, t is the time, V is the voltage, and w is the total weight of a pair of disk electrodes.

Electronic structure calculations.— Geometries were optimized at the HF and PBE1PBE levels of theory combined with the aug-cc-pVTZ basis set using the program Gaussian 03.[35] Molecular volumes were calculated using the Monte Carlo method as implemented in Gaussian 03.

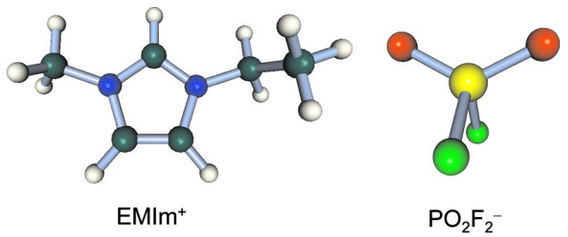

Figure 1. (Color online) Structures of the 1-ethyl-3-methylimidazolium cation ($EMIm^+$) and difluorophosphate anion ($PO_2F_2^-$).

Results and Discussion

Electric double-layer capacitance.— Table I summarizes the physical properties of $EMImPO_2F_2$ and $EMImBF_4$ used in the current study. The melting point of $EMImPO_2F_2$ (280 K) is slightly lower than that of $EMImBF_4$ (288 K), and the conductivity and viscosity of $EMImPO_2F_2$ are comparable to those of $EMImBF_4$.[34,36] Figure 2 shows the charge–discharge curves obtained for $EMImPO_2F_2$, together with those obtained for $EMImBF_4$ for comparison. In the $EMImPO_2F_2$, the voltage increase in the charge curve becomes sluggish at a charging voltage of 3.0 V, and the deformation of the discharge curve becomes apparent at a charging voltage of 3.5 V. The charge and discharge curves for $EMImPO_2F_2$ at a charging voltage of 4.0 V are totally deformed. The deterioration of the electrolyte causes such behavior and results in the increase in the internal resistance, as shown in the increase in the IR drop. Figure 3 shows the voltage dependence of capacitance for the EDLC using $EMImPO_2F_2$ together with that using $EMImBF_4$ as the electrolyte for comparison. The charging voltage was increased from 1.0 to 4.0 V by a 0.1 V step. Overall, the capacitance of $EMImPO_2F_2$ exhibits a higher voltage dependence than that of $EMImBF_4$, leading to the higher capacitance of $EMImPO_2F_2$ at the charging voltages above 1.5 V. Although the origin of this behavior is not clear, the asymmetric $PO_2F_2^-$ might change the orientation on the electrode at high voltages. The capacitance obtained for $EMImPO_2F_2$ is 49 F g^{-1} and is higher than 44 F g^{-1} for $EMImBF_4$ when the cell is charged at 2.5 V. The capacitance of EDLCs using activated carbon electrodes and BF_4^--based ionic liquids is usually higher than those using other ionic liquids such as PF_6^-- and $N(SO_2CF_3)_2^-$-based ones.[8,11] The larger capacitance of $EMImPO_2F_2$ compared to that of $EMImBF_4$ is considered to arise from the characteristics of $PO_2F_2^-$. The obvious difference between $PO_2F_2^-$ and BF_4^- in terms of molecular geometry is their symmetry. The $PO_2F_2^-$ anion has a C_{2v} symmetry with a dipole moment and a more negative charge on the oxygen atoms than the fluorine atoms, while the BF_4^- has a higher symmetry of T_d. Such a difference in molecular geometry may affect the structure of the electric double layer and may result in the different voltage dependence of capacitance. According to the quantum mechanical calculation at PBE1PBE/aug-cc-pVTZ, the molecular volume of $PO_2F_2^-$ (85 Å^3) is between the two popular fluorocomplex anions used for ionic liquid electrolytes, BF_4^- (74 Å^3) and PF_6^- (97 Å^3) (Fig. 4). The size of $PO_2F_2^-$ may be another factor for its high capacitance. In the region above the charging voltage of 3.0 V, the capacitance of $EMImPO_2F_2$ is increased steeply, which is ascribed to the decomposition of the electrolyte, whereas the capacitance of $EMImBF_4$ exhibits almost a linear increase in this region.

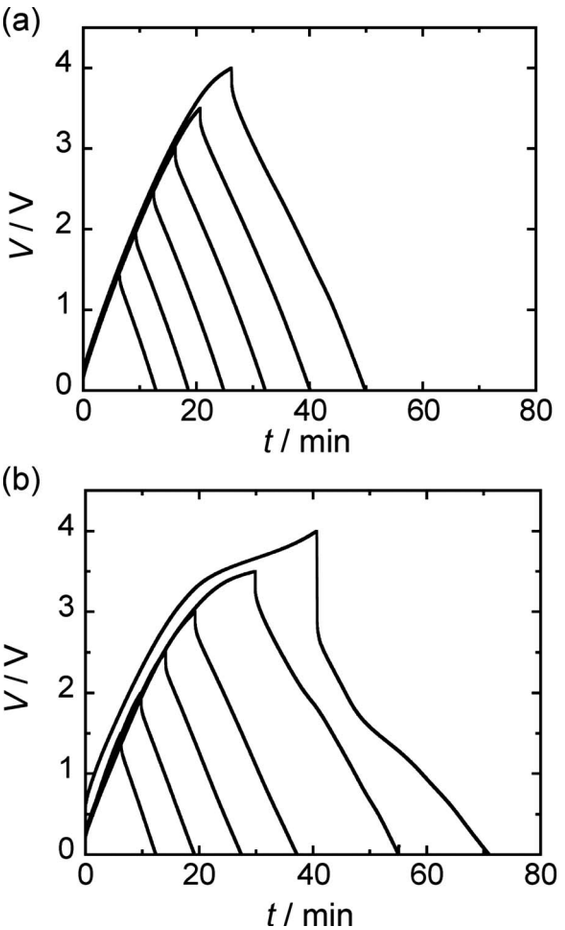

Figure 2. Charge–discharge curves of EDLCs using (a) $EMImBF_4$ and (b) $EMImPO_2F_2$.

Figure 5 shows the capacitance and coulomb efficiency of the EDLCs using (a) $EMImPO_2F_2$ and (b) $EMImBF_4$ as a function of cycle number, where the charging voltage was increased every 50th cycle by 0.5 V from 2.0 to 3.5 V. The capacitance loss during the cycles at 2.0 and 2.5 V is quite small in both the cases of $EMImPO_2F_2$ and $EMImBF_4$. The capacitance of $EMImPO_2F_2$ slightly decreases during the cycles at 3.0 V and significantly drops during the cycles at 3.5 V, whereas the capacitance of $EMImBF_4$ is constant during the cycles at 3.0 V, and slightly decreases as the cycle proceeds at 3.5 V. The drop in the coulomb efficiency at the high charging voltage is more evident for $EMImPO_2F_2$ than that for $EMImBF_4$. These results indicate the lower electrochemical stability

Table I. Physical and thermal properties of the ionic liquids in the current study.

	$T_m(T_g)$ (K)	ρ/g (cm^{-3})	MV (cm^3 mol^{-1})	η (mPa s)	σ (mS cm^{-1})	Λ (S cm^2 mol^{-1})	C (F g^{-1})	Ref.
$EMImPO_2F_2$	280	1.31	161	35	12	1.9	49	34
$EMImBF_4$	288 (194)	1.27	156	34	13	2.0	44	36

T_m: melting point, T_g: glass transition temperature, ρ: density at 298 K, MV: molar volume at 298 K, η: viscosity at 298 K, σ: ionic conductivity at 298 K, Λ: molar conductivity at 298 K, and C: capacitance obtained for the present EDLC cell at the charging voltage of 2.5 V.

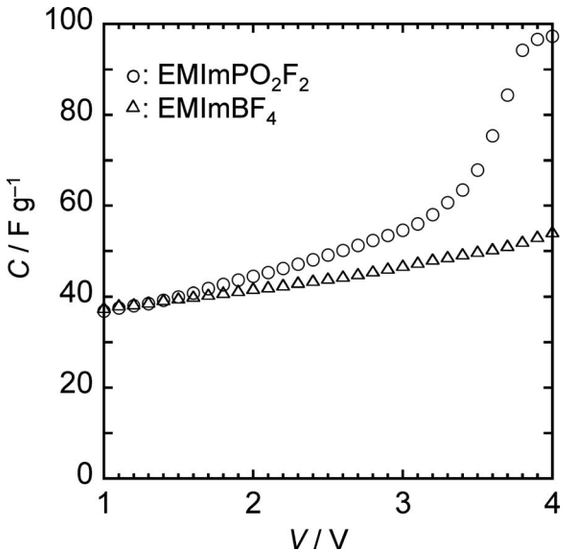

Figure 3. Voltage dependence of capacitance for $EMImPO_2F_2$ and $EMImBF_4$.

of $EMImPO_2F_2$ compared to that of $EMImBF_4$ in the present EDLC cell. Although there may be several factors on this point including the reaction of the electrolyte and surface functional groups on the activated carbon electrode, the difference in the anodic stability is considered to be one of the possible reasons, as shown below.

Anodic stability of $PO_2F_2^-$.— Figure 6 shows the comparison of the electrochemical stability between $EMImPO_2F_2$ and $EMImBF_4$ by using the linear sweep voltammetry of a vitreous carbon electrode. The voltammetric curves for the two ionic liquids completely overlap at the cathode limit (−2.5 V vs Fc^+/Fc, where the current density is 0.5 mA cm^{-2}), suggesting the decomposition of the cationic species. The anode limit of $EMImPO_2F_2$ is lower than that of $EMImBF_4$ by 0.3 V, which arises from the difference in the stability of the anions against oxidation. The anodic stability of typical anionic species for the electrolytes in the organic solvents and for the ionic liquid electrolytes was experimentally determined on a vitreous carbon electrode,[37,38] although such anions are often intercalated into graphitized materials at lower potentials.[39-42] Theoretical works to evaluate the anodic stability were performed by calculating the ionization potential of the anions.[37,43-45] The evaluation using the highest occupied molecular orbital energy (E_{HOMO}) is based on Koopmans' theorem and is valid only at the HF level. The vertical ionization potential (E_v) is also used for this purpose and is calculated from the energy difference between the total energy of the anion and that of the neutral radical without geometry optimization (the same geometry as the optimized geometry for the corresponding anion) based on the Franck–Condon principle. These calculations provide the order of the anodic stability of the anions. Table II lists E_{HOMO} at HF/aug-cc-pVTZ and E_v at PBE1PBE/aug-cc-pVTZ calculated for $PO_2F_2^-$ with the values for PF_6^-, BF_4^-, and ClO_4^- for

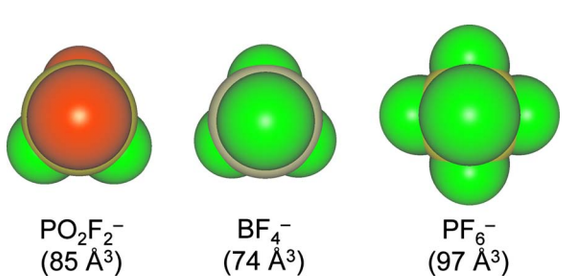

Figure 4. (Color online) Space filling models of $PO_2F_2^-$, BF_4^-, and PF_6^-. The volumes calculated at PBE1PBE/aug-cc-pVTZ are given in parentheses.

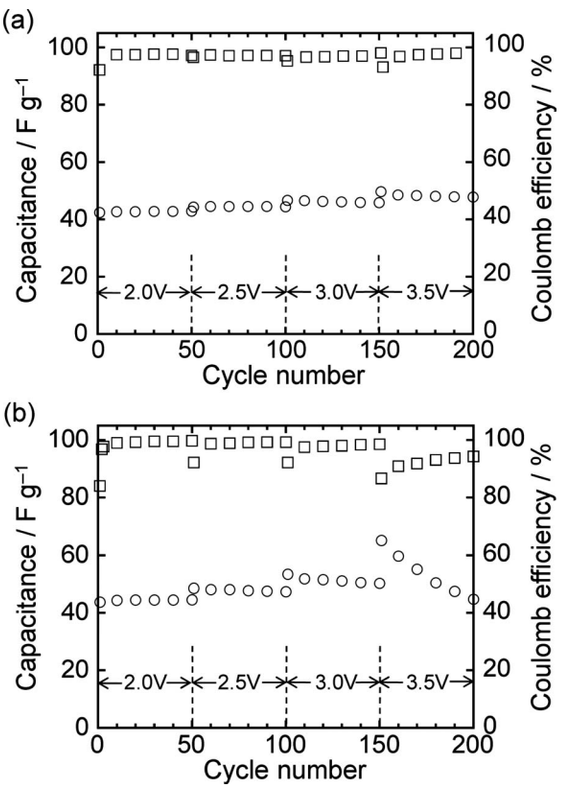

Figure 5. The capacitance (○) and coulomb efficiency (□) of the EDLCs using (a) $EMImBF_4$ and (b) $EMImPO_2F_2$ as a function of cycle number, where the charging voltage was increased every 50th cycle by 0.5 V from 2.0 to 3.5 V.

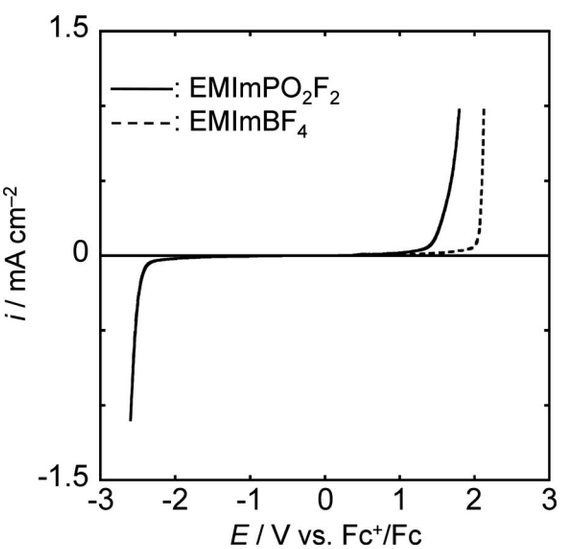

Figure 6. Linear sweep voltammograms of a vitreous carbon electrode in $EMImPO_2F_2$ and $EMImBF_4$. Scan rate: 5 mV s^{-1}, counter electrode: Pt wire, and reference electrode: Ag wire immersed in $EMImBF_4$ containing 0.05 M $AgBF_4$. The potential is referenced to the redox potential of the Fc^+/Fc couple.

Table II. E_{HOMO} and E_v for $PO_2F_2^-$, BF_4^-, PF_6^-, and ClO_4^-.

	E_{HOMO} [a] (eV)	E_v [b] (eV)
$PO_2F_2^-$	−7.3	−5.3
BF_4^-	−10.3	−7.3
PF_6^-	−11.0	−8.0
ClO_4^-	−7.4	−5.5

[a] E_{HOMO} was calculated at HF/aug-cc-pVTZ.
[b] E_v was calculated at PBE1PBE/aug-cc-pVTZ.

comparison. In both the methods, the ionization potentials obtained in this study increases in the order of $PO_2F_2^- \approx ClO_4^- < BF_4^- < PF_6^-$. The low stability of ClO_4^- against oxidation compared to the common inorganic fluoroanions was already pointed out in previous studies.[38,43] The present calculations proved that the anodic stability of $PO_2F_2^-$ is similar to that of ClO_4^- and validated the lower breaking-up voltage of the EDLC using $EMImPO_2F_2$ than that using $EMImBF_4$.

Conclusion

In this study, the performance of the EDLC using $EMImPO_2F_2$ was measured and compared with that using $EMImBF_4$. The high capacitance observed for $EMImPO_2F_2$ is attractive in the practical use. The breaking-up voltage of the EDLC using $EMImPO_2F_2$ is lower than 3.0 V, which may be explained by the lower anodic stability of $PO_2F_2^-$ than the typical fluorocomplex anions such as BF_4^-.

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